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Lower and upper limits to the vibrational thermal conductivity of amorphous polymers and polymer salts

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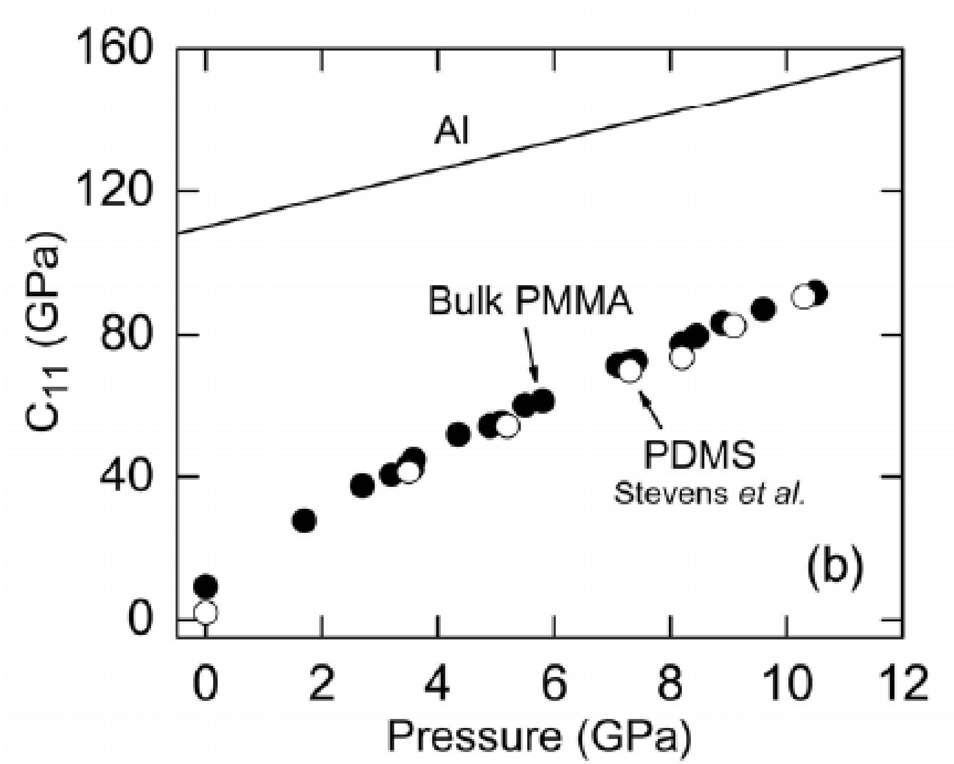
Outline

- Structure/property relationships for amorphous polymers. Search for…
  - High thermal conductivity. Increase the strength of interchain bonding; extension to ionomers
  - Low thermal conductivity. Introduce cage-structure side groups

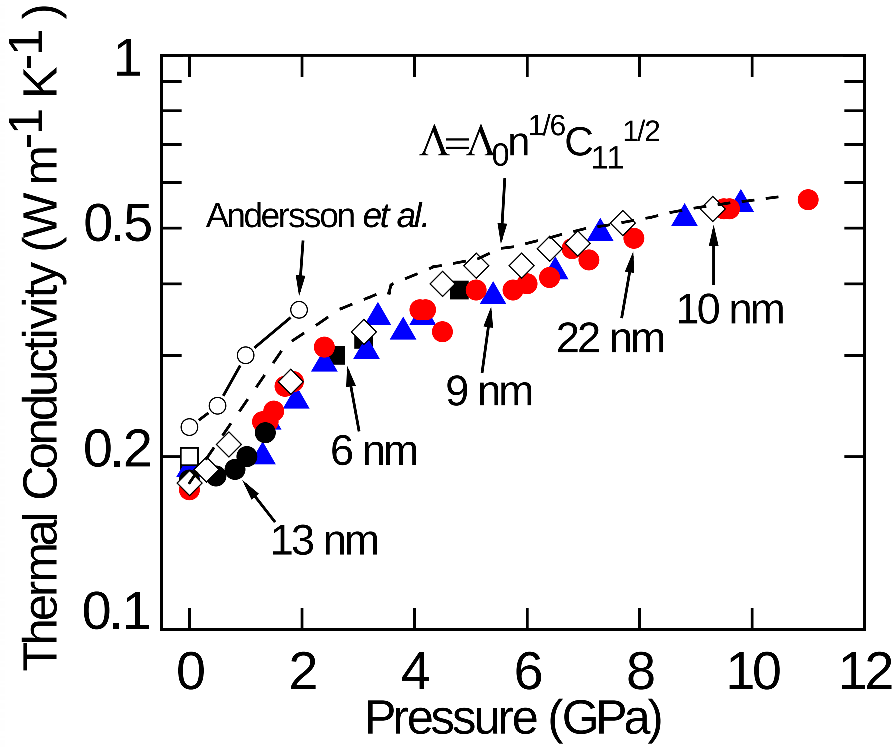
- Explore thermal function in macromolecules
  - Thermal switching in liquid crystal networks.

Prior work on thermal conductivity and elastic constants of a glassy polymer, PMMA, in a SiC anvil cell

- Thermal conductivity doubles at a pressure of ≈5 GPA when the elastic modulus reaches C_{11}≈50 GPA



Stevens *et al.*, J. Chem. Phys. 127 104906 (2007)

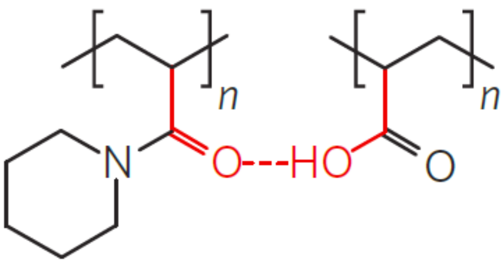


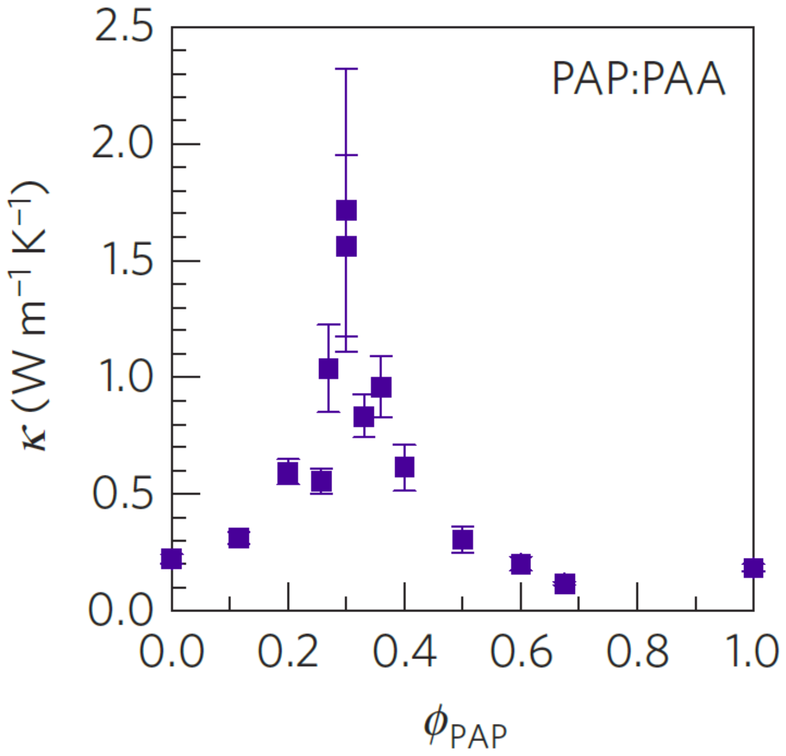
Hsieh et al, PRB (2011)

2015 report of anomalously high thermal conductivity in hydrogen-bonded polymer blends

- We were unable to reproduce this result. (PAP and PAA phase separate?)
- Continue the same basic idea: how much can we increase the thermal conductivity of an amorphous polymer by increasing the inter-chain bonding strength?

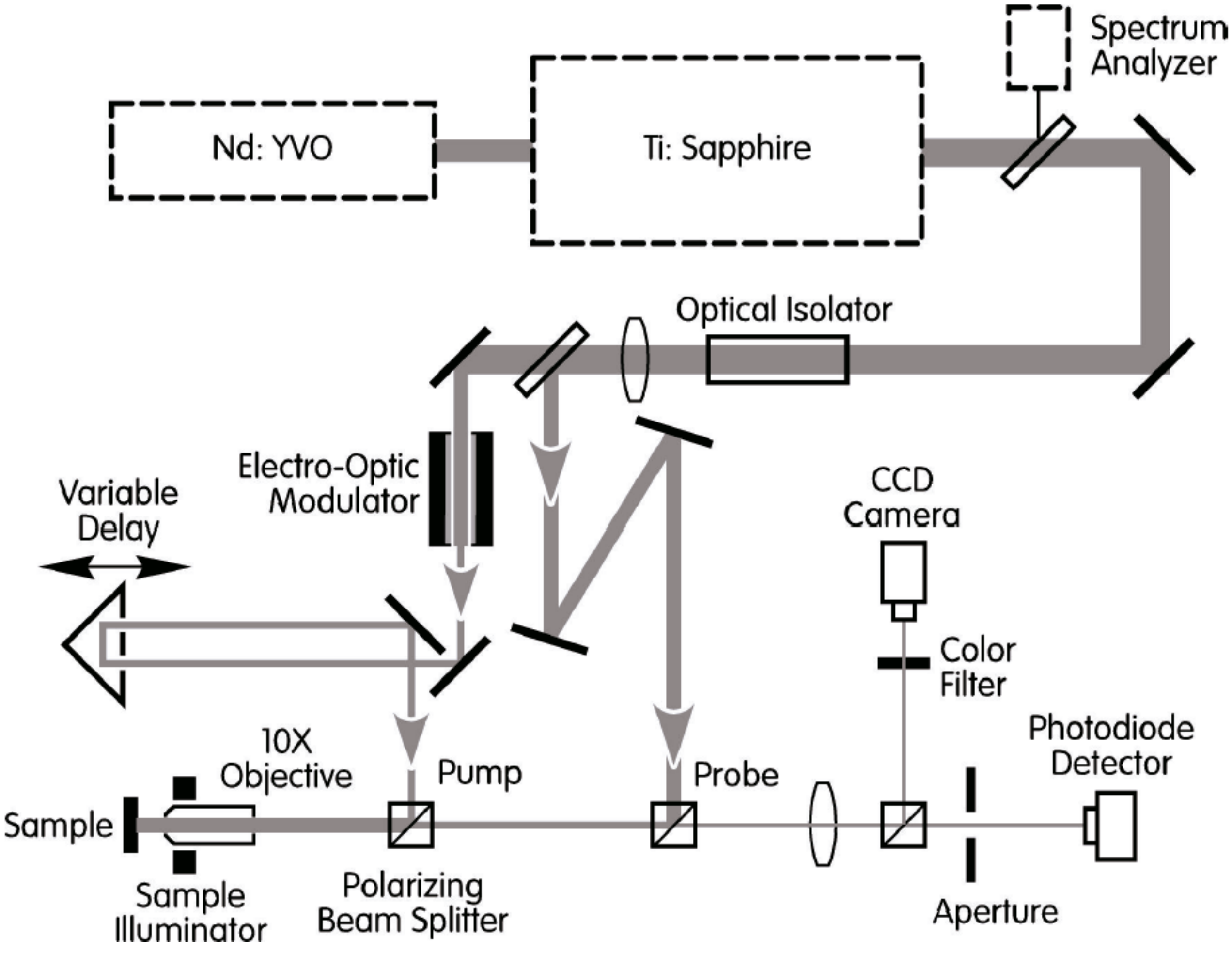
PAP:PAA





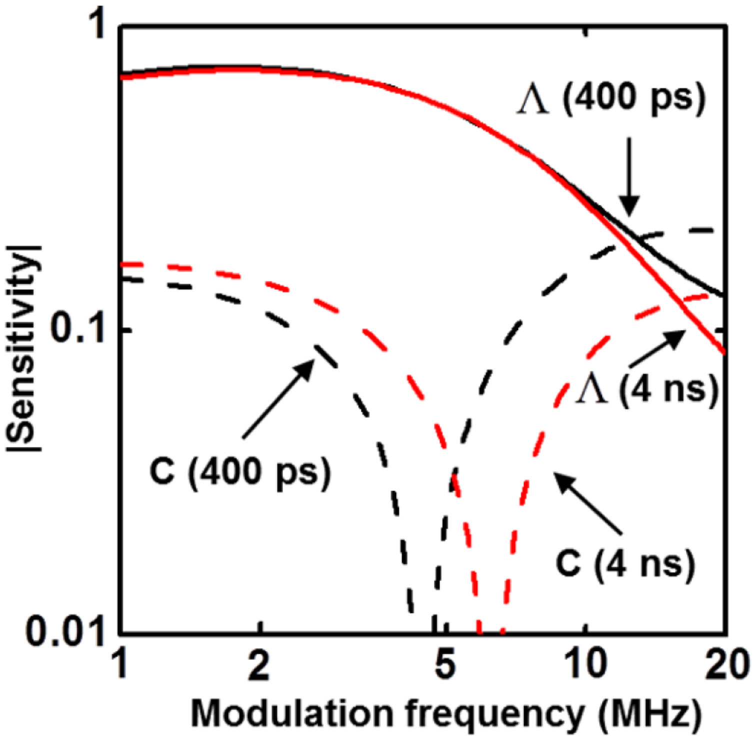
Kim *et al.*, Nature Materials (2015)

Pump-probe measurements thermal properties and elastic constants



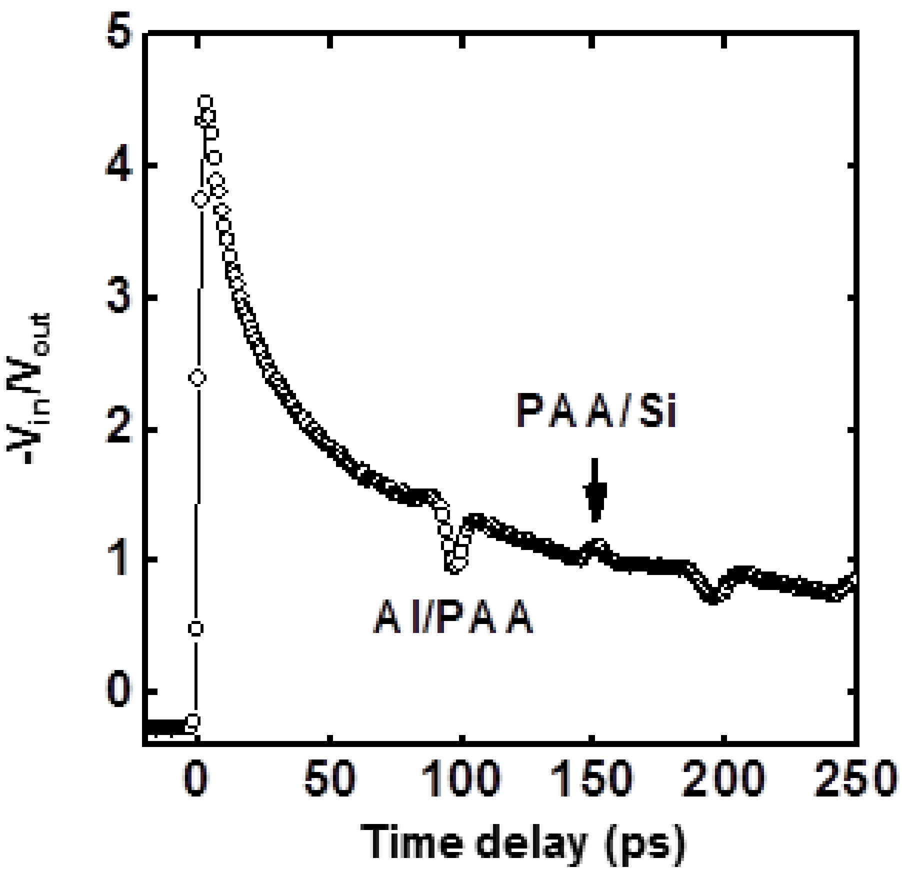
Measure thermal conductivity Λ and heat capacity *C* of thin films using time-domain thermoreflectance at multiple modulation frequencies *f*

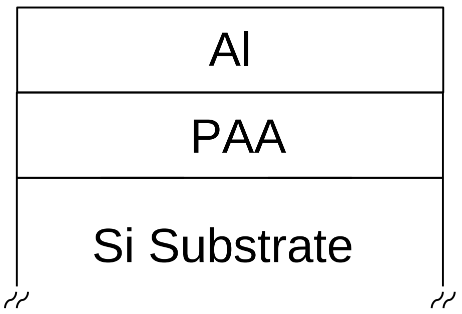
- Sensitivities for 100 nm thick polymer layer on a Si substrate and coated with 90 nm of Al.
- Fit data acquired at f=1.6, 4.1 and 9.1 MHz



Xie *et al.*, Macromolecules (2016)

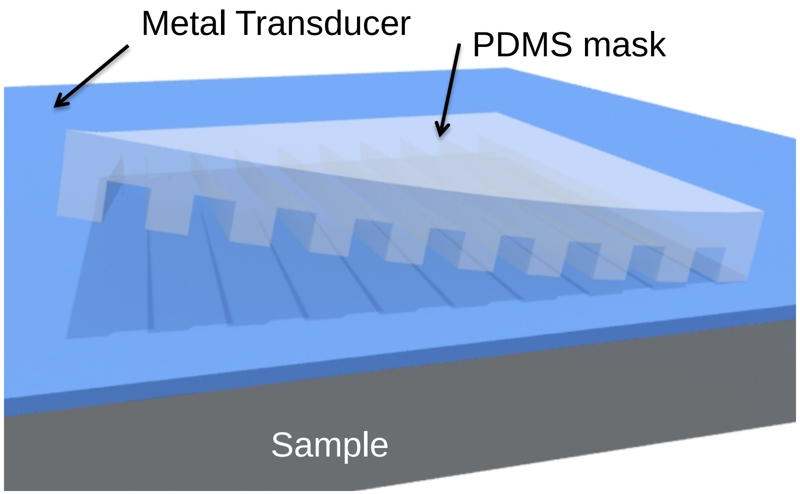
Measure longitudinal sound velocity using conventional picosecond acoustics

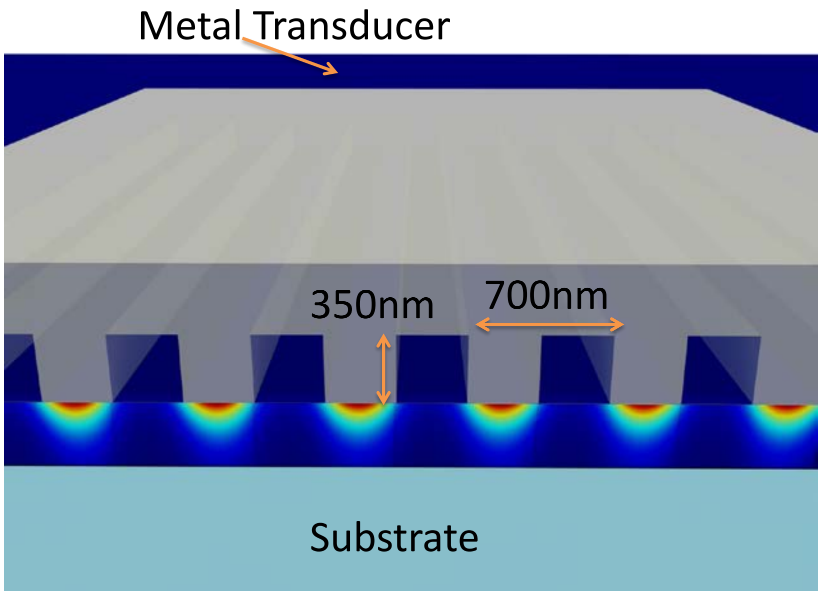


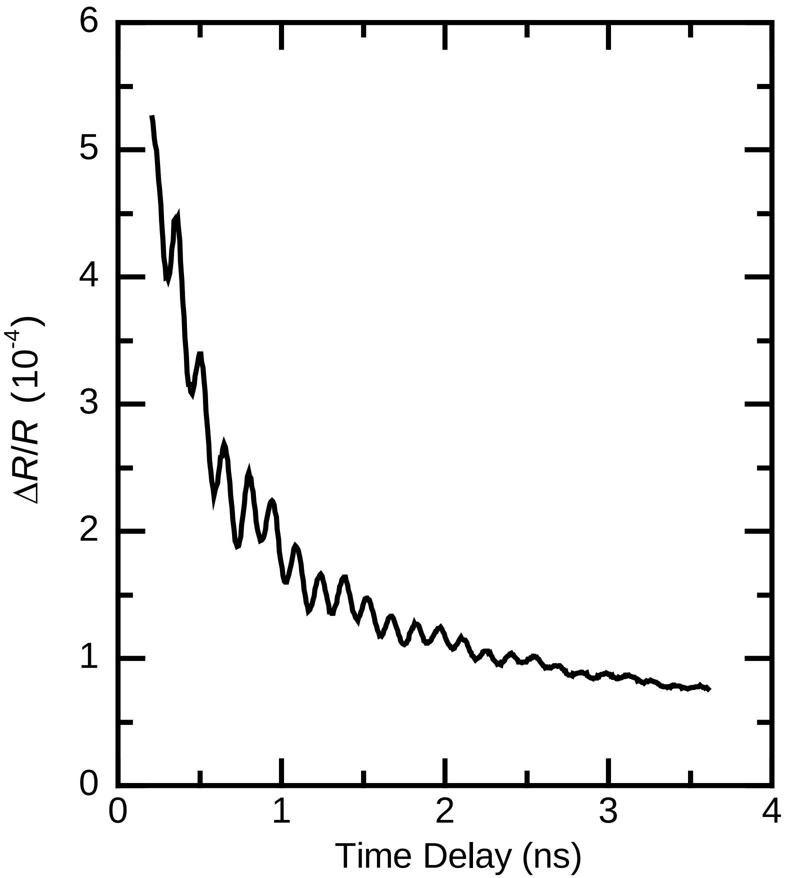


Xie *et al.*, Macromolecules (2016)

Measure surface acoustic wave velocity using elastomeric phase shift mask

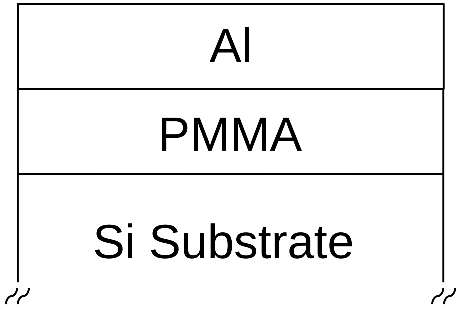






Li *et al.*, J. Appl. Phys. (2013)

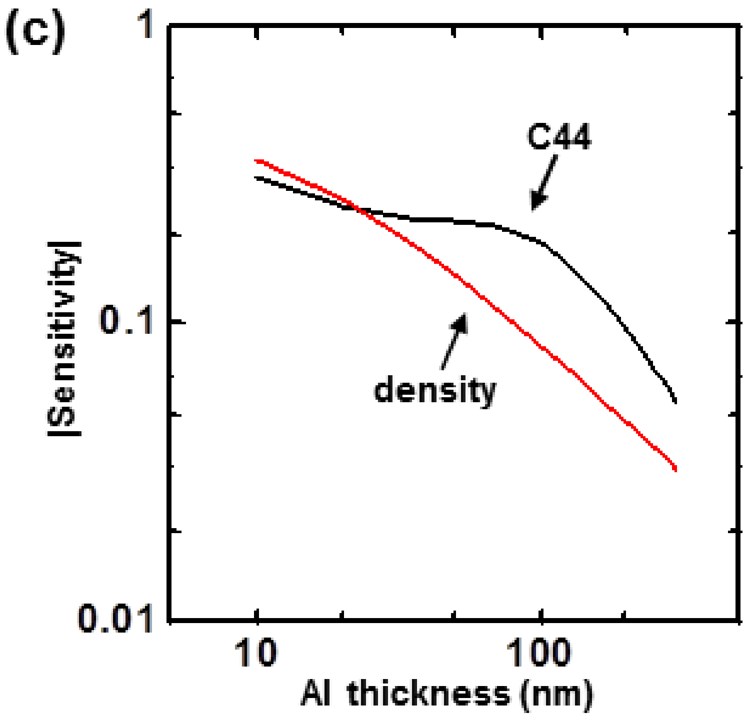
Experimental details: need to optimize thickness of sample and metal transducer



- Example sensitivity calculations for Al/PMMA(100nm)/Si

$$S = \frac{c_{44}}{v_{SAW}} \frac{\partial v_{SAW}}{\partial c_{44}}$$

- Approach fails if the Al transducer is too thin or if the PMMA layer is too thick.

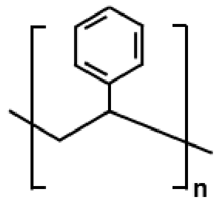


Xie *et al.*, Macromolecules (2016)

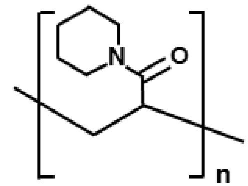
Study macromolecules with various interchain bonding types

Weak interaction

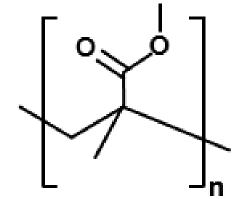
Van der Waals bond



Polystyrene
(PS)

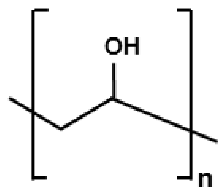


Poly(acryloyl piperidine)
(PAP)

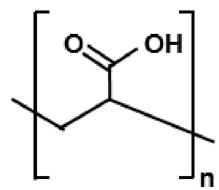


Poly(methyl methacrylate)
(PMMA)

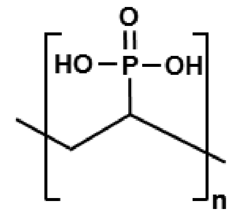
hydrogen bond



Poly(vinyl alcohol)
(PVA)

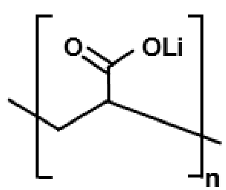


Poly(acrylic acid)
(PAA)

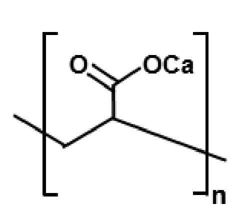


Poly(vinylphosphonic acid)
(PVPA)

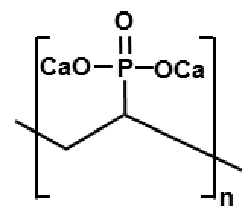
Ionic bond



PALi



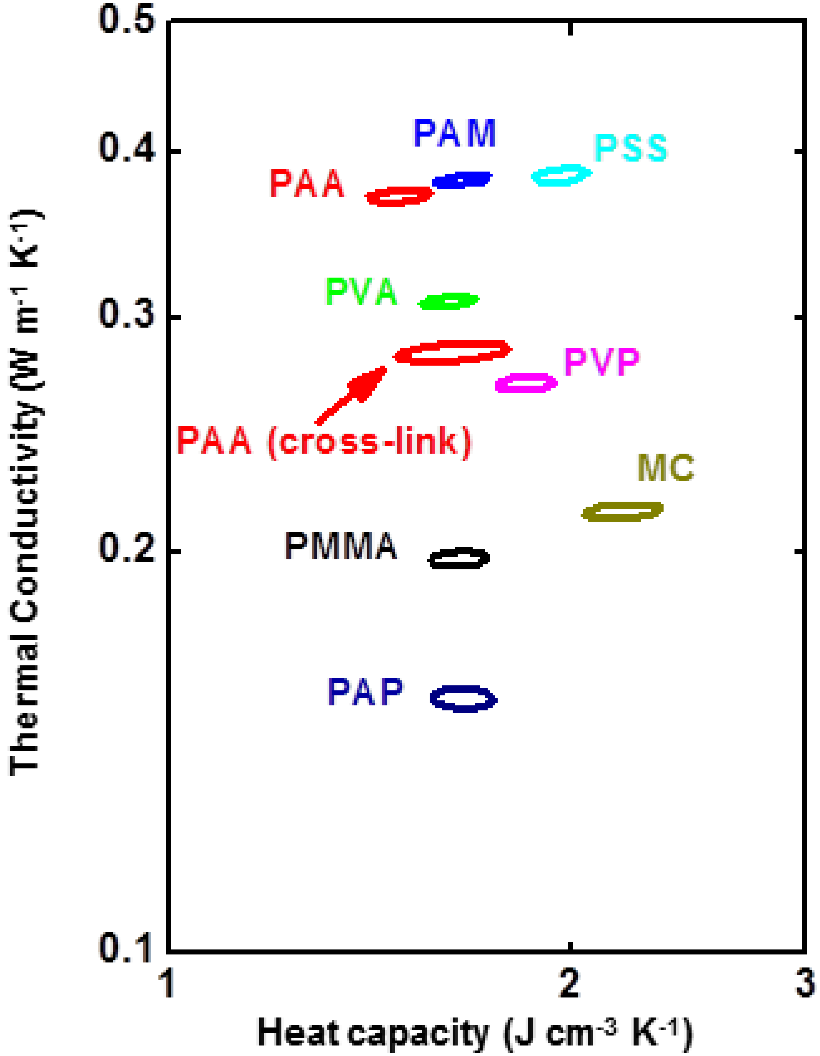
PACa

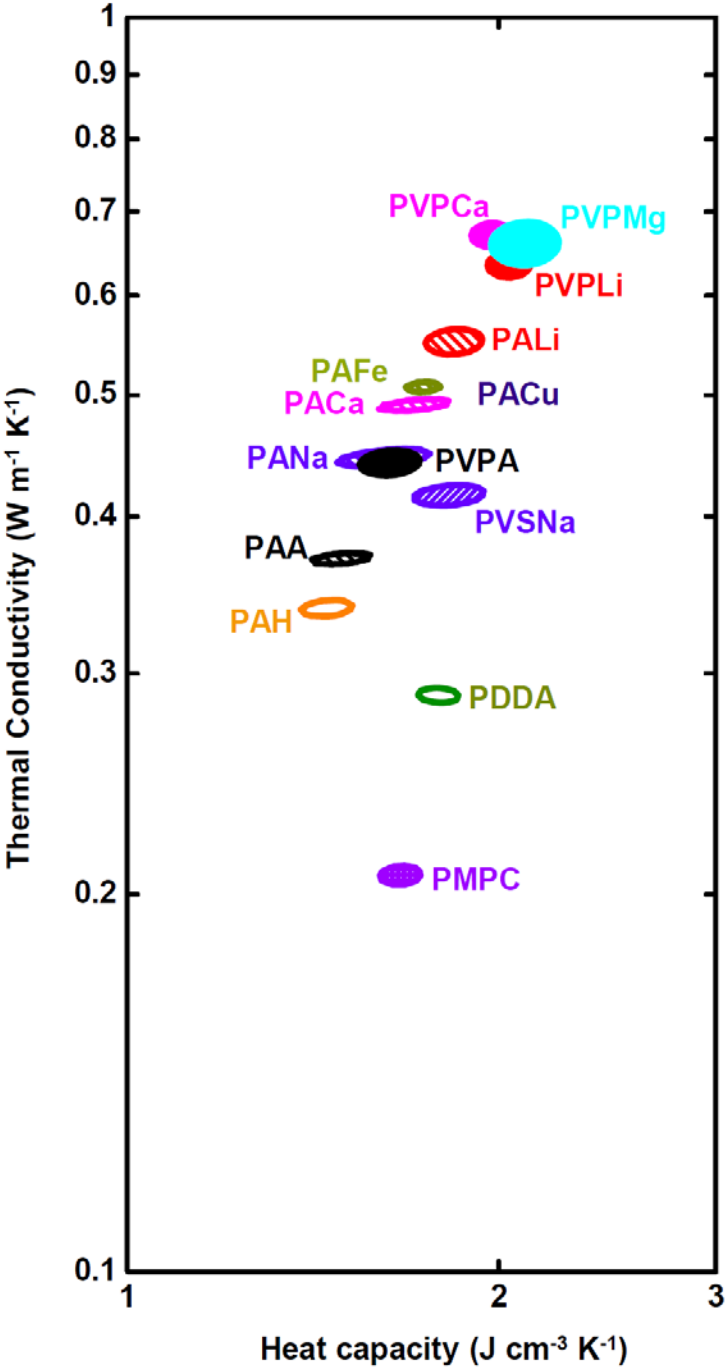


PVPCa

Strong interaction

95% confidence intervals for Λ and C

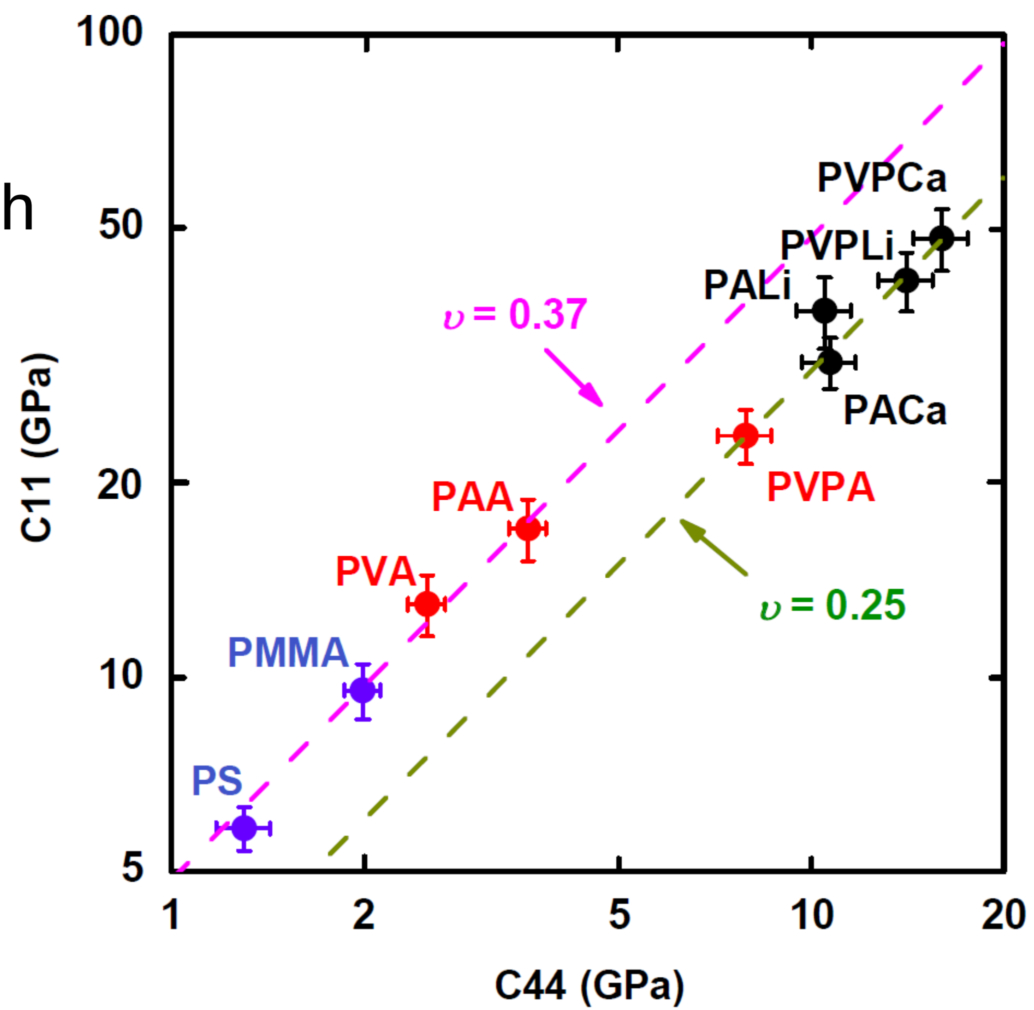




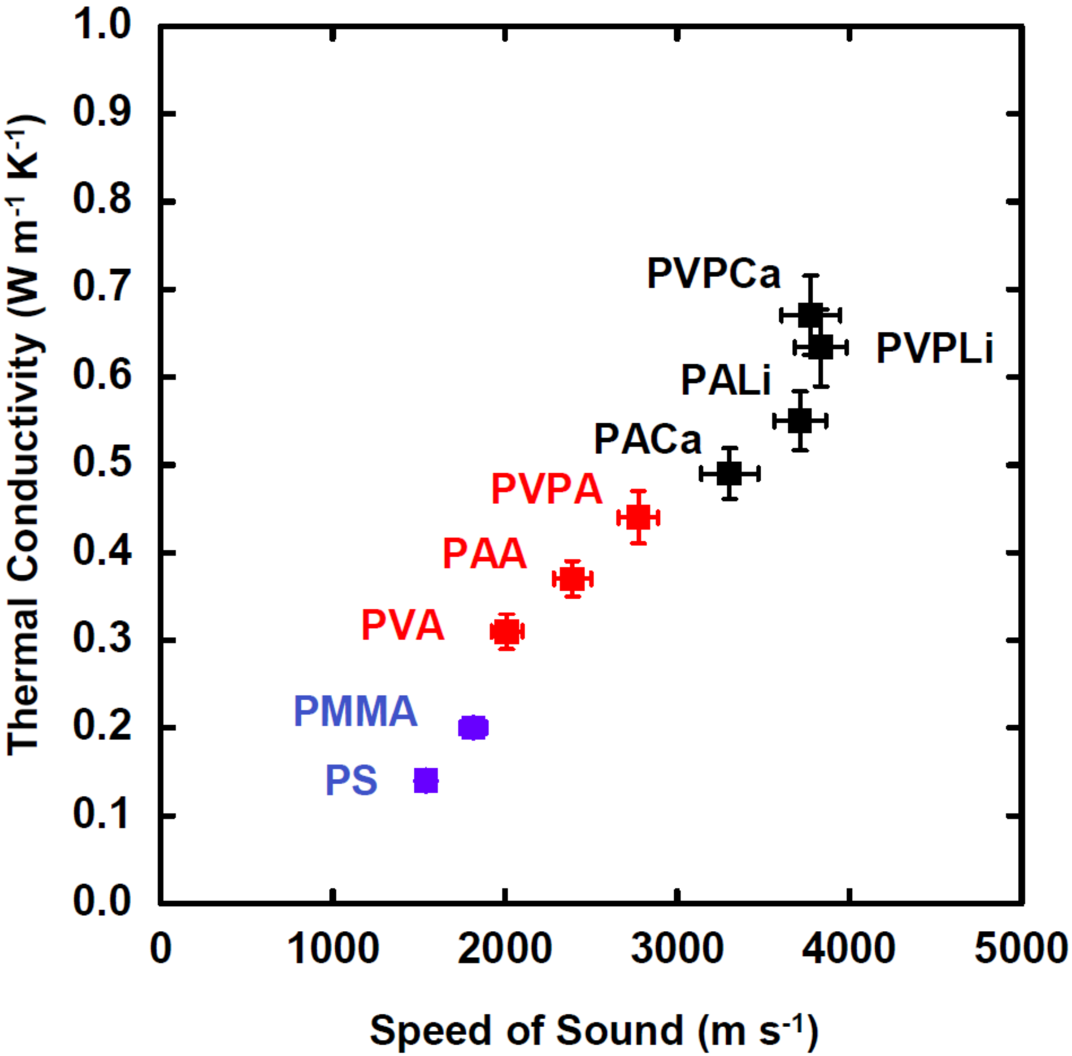
Xie *et al.*, Macromolecules (2016)

Elastic constants span an order of magnitude. Transition in Poisson ratio?

- Poisson ratio is ν≈0.37 for polymers with small elastic constants and ν≈0.25 for polymers with large elastic constants.

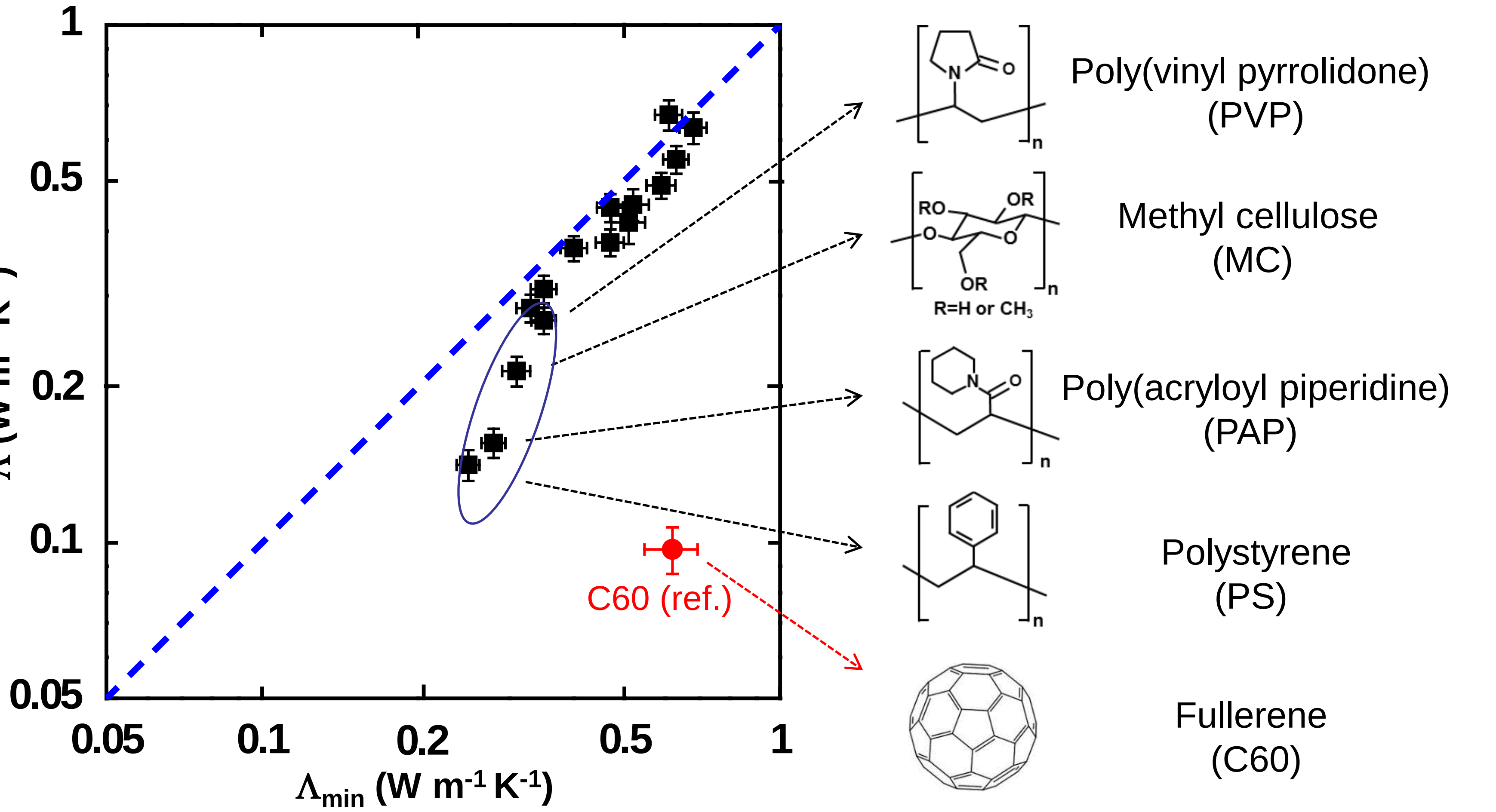


Model of minimum thermal conductivity predicts a correlation with average speed of sound

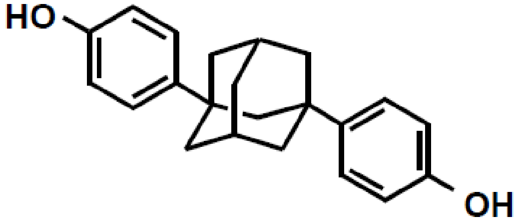


Make the comparison quantitative by introducing a density of vibrational states $n_c = (2/3)(n - n_H)$

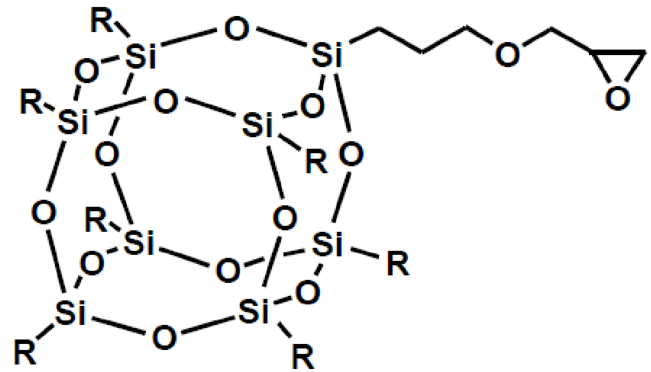
$$\Lambda_{\min} = \left(\frac{9\pi}{16}\right)^{1/3} k_B n_c^{2/3} \overline{V} \qquad \overline{V} = \frac{1}{3}\left(v_l + 2v_t\right)$$



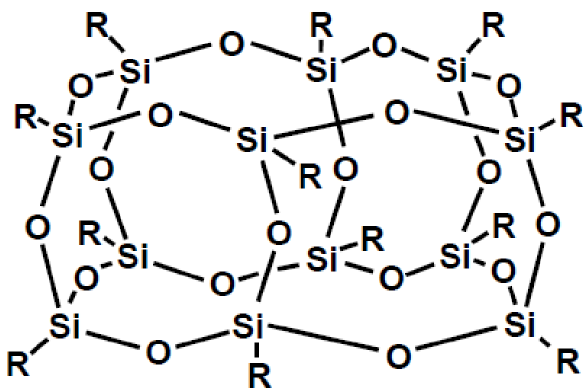
Search for low thermal conductivity with cage-structured molecules

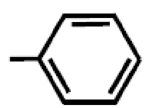


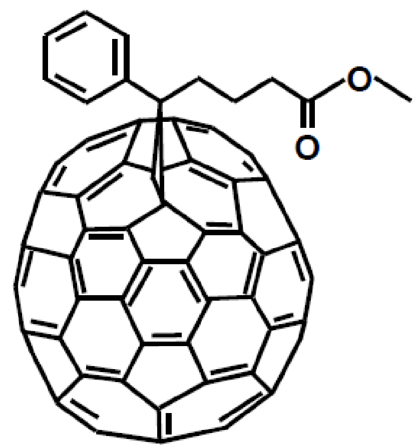
ADP



GHSQ R= 

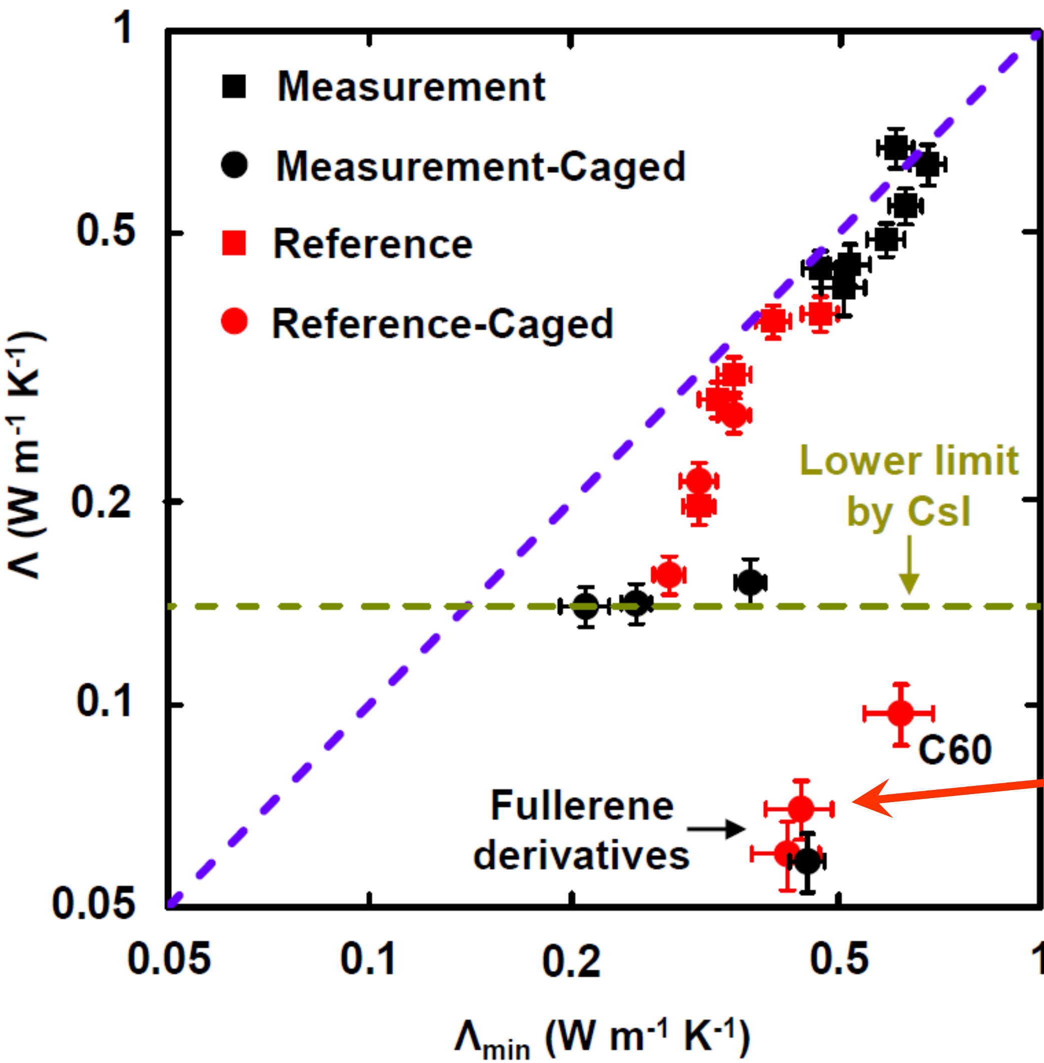


DSQ R= 



PC71BM

Fullerene derivatives have ultralow thermal conductivity

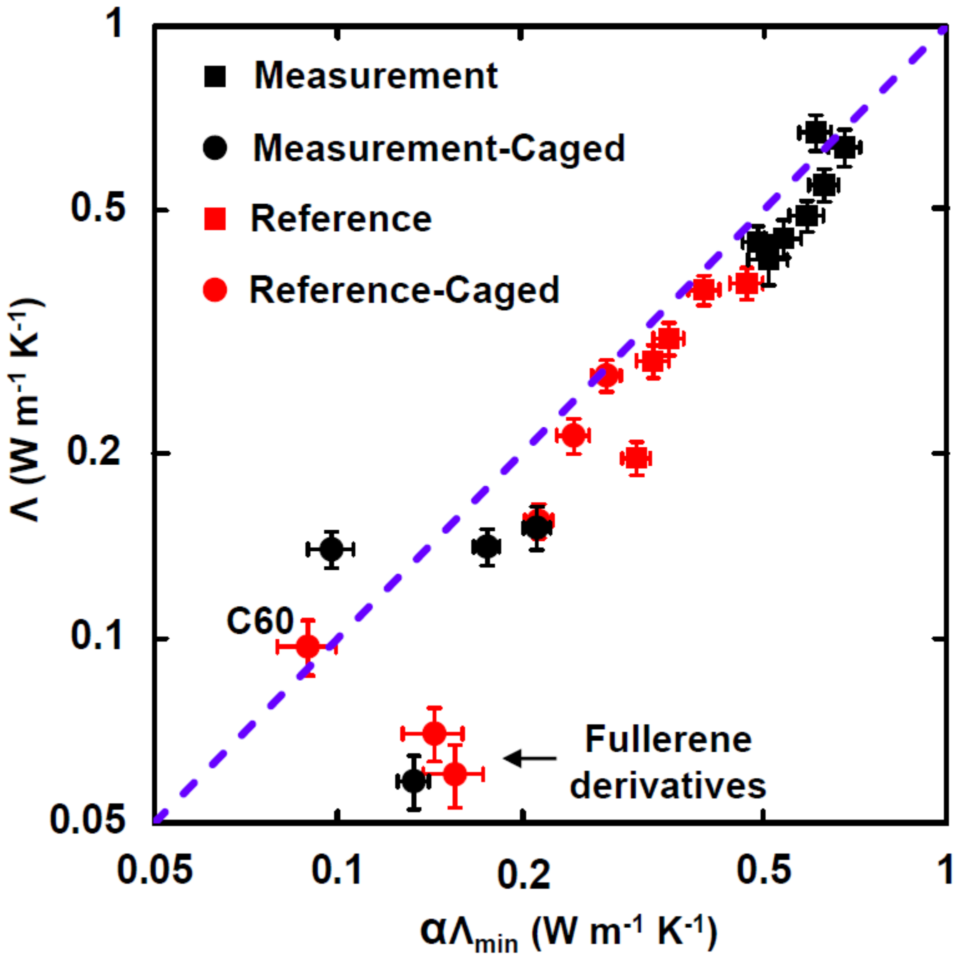


- Search of an elastic constants database led us to CsI: the inorganic solid with the lowest Λ_{min} at room temperature.

- UIUC prior work, Wang et al., PRB (2013) on C_{60} fullerene derivatives.

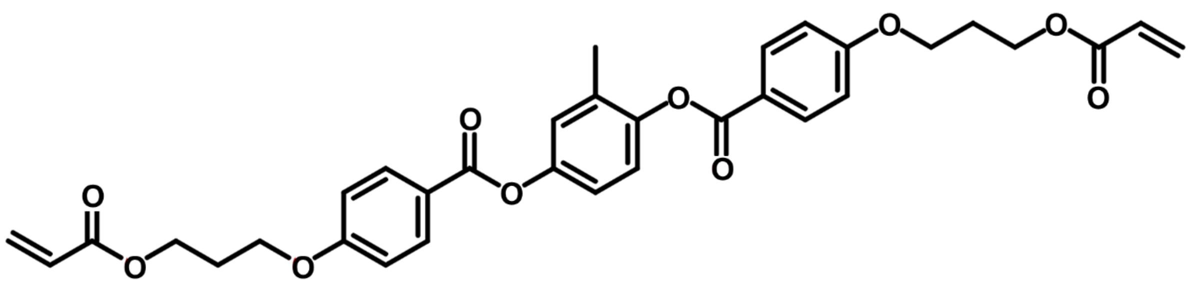
Multiply prediction by a factor α to take into account vibrational modes localized to the cage structure

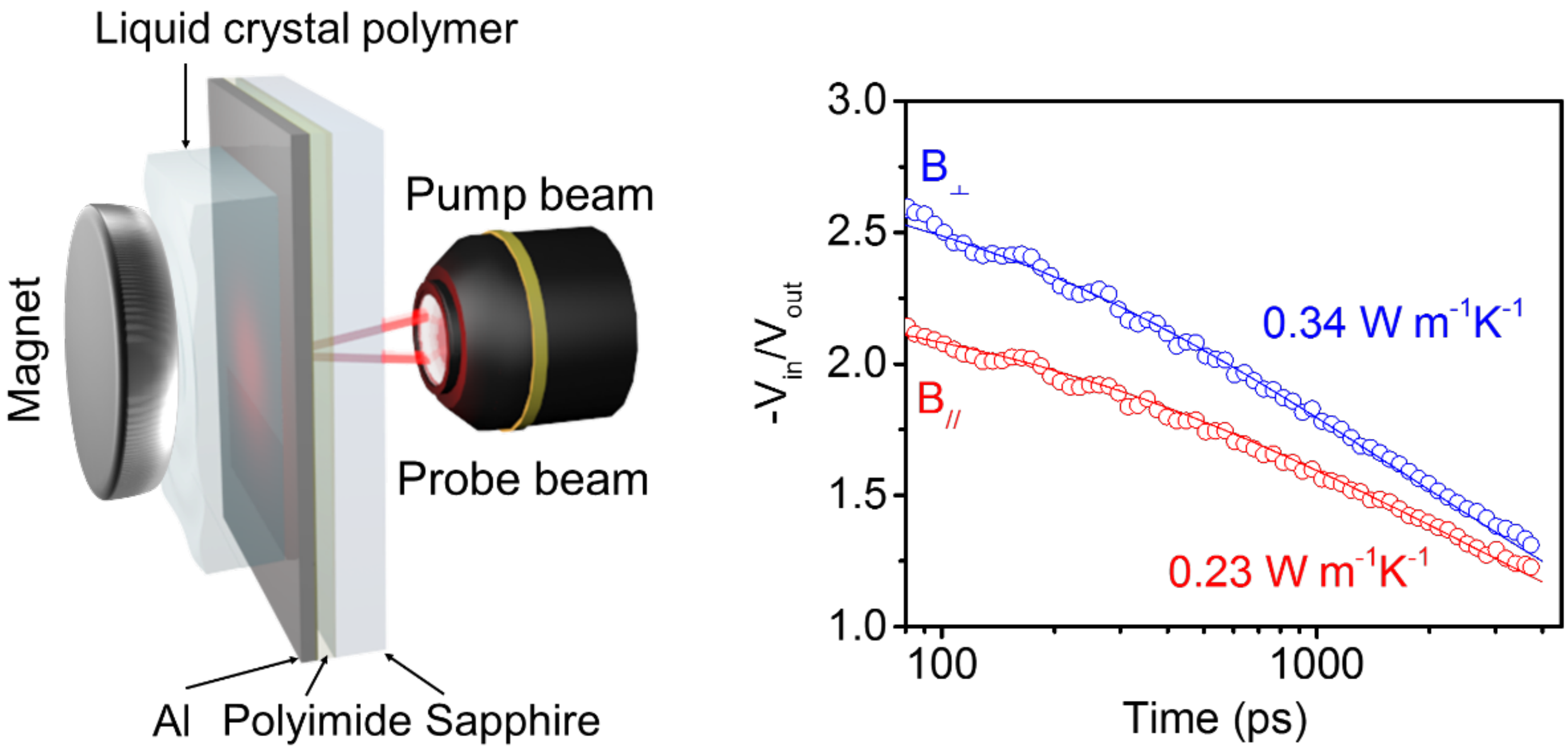
n_{eff} is calculated by treating each cage structure as 5/3 of an atom



$$\alpha = \left(\frac{n_{eff}}{n_c} \right)^{2/3}$$

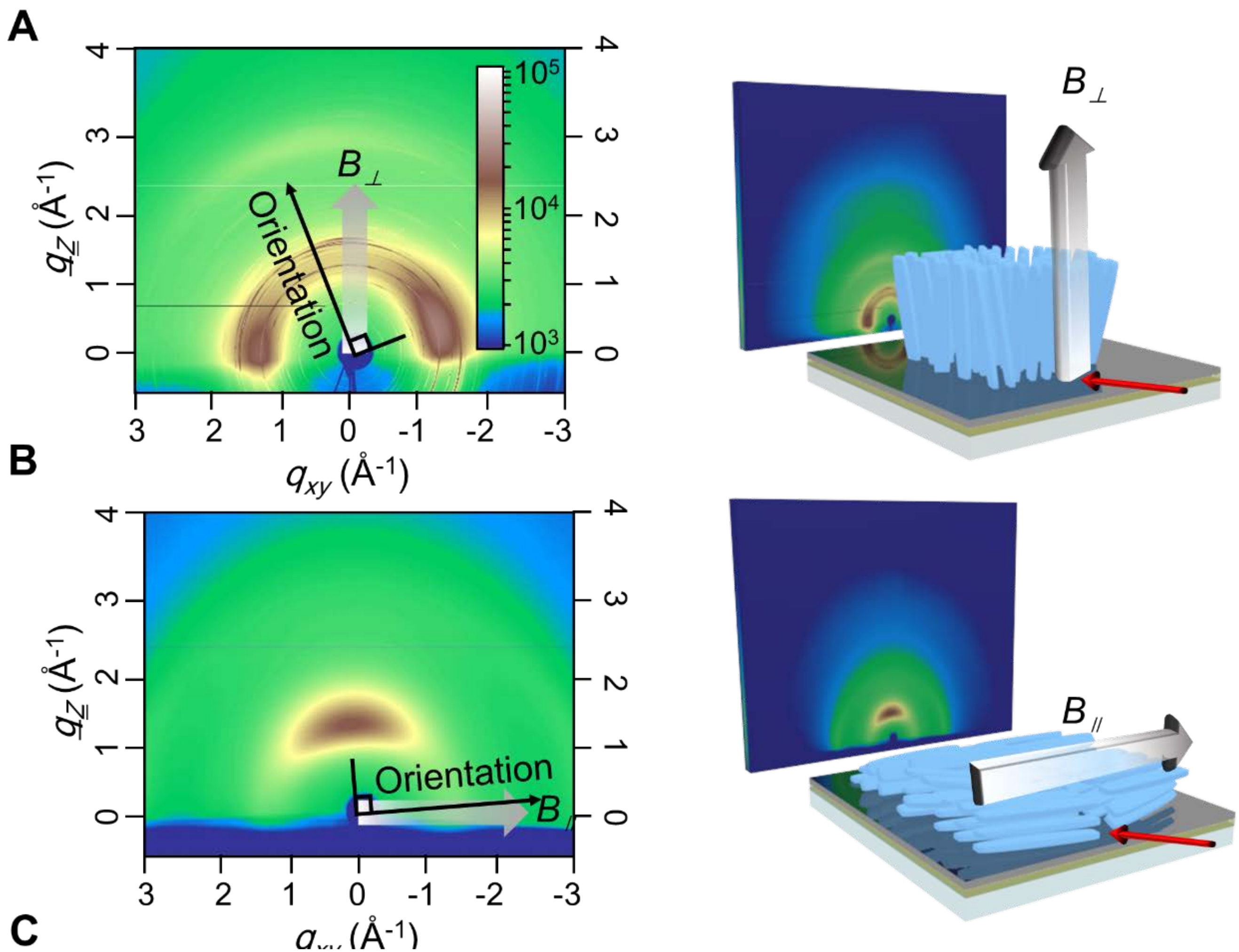
Magnetic-field aligned photopolymerization of liquid crystal RM257 monomer





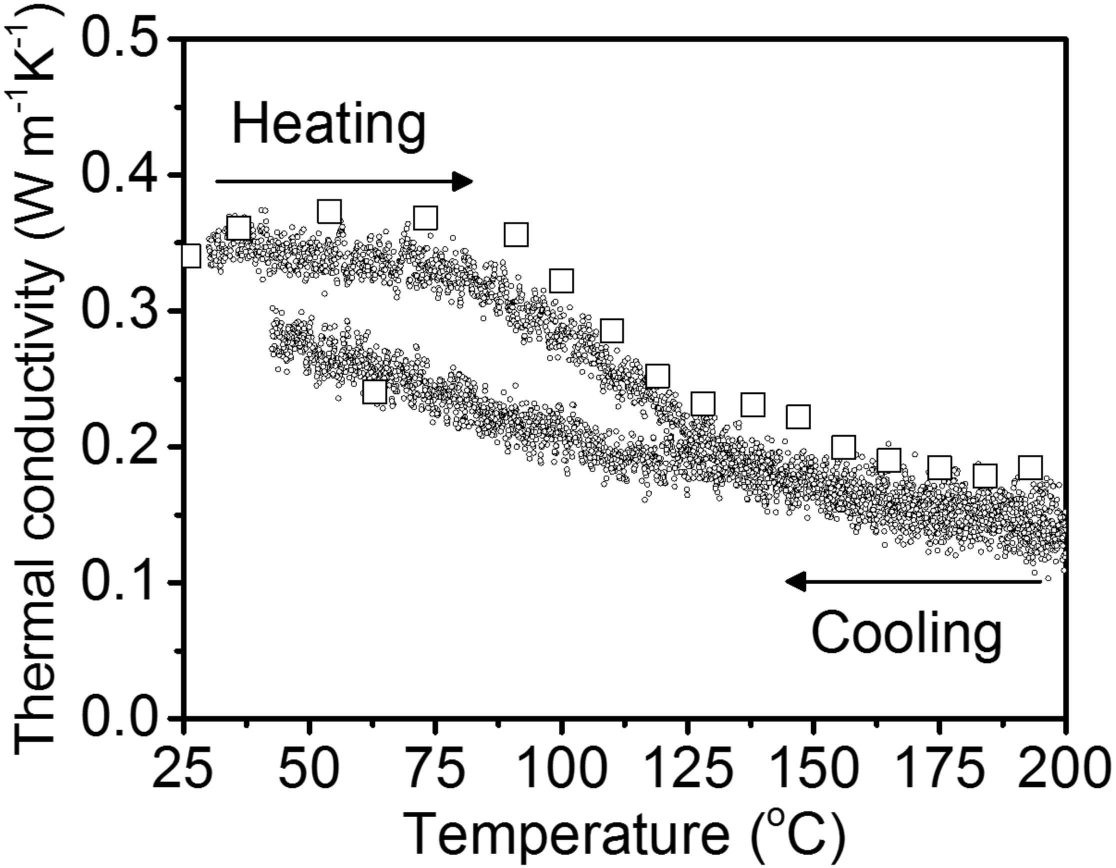
Shin *et al.*, Macro Letters (2016)

Analyze order parameter from x-ray scattering data at APS



Shin *et al.*, Macro Letters (2016)

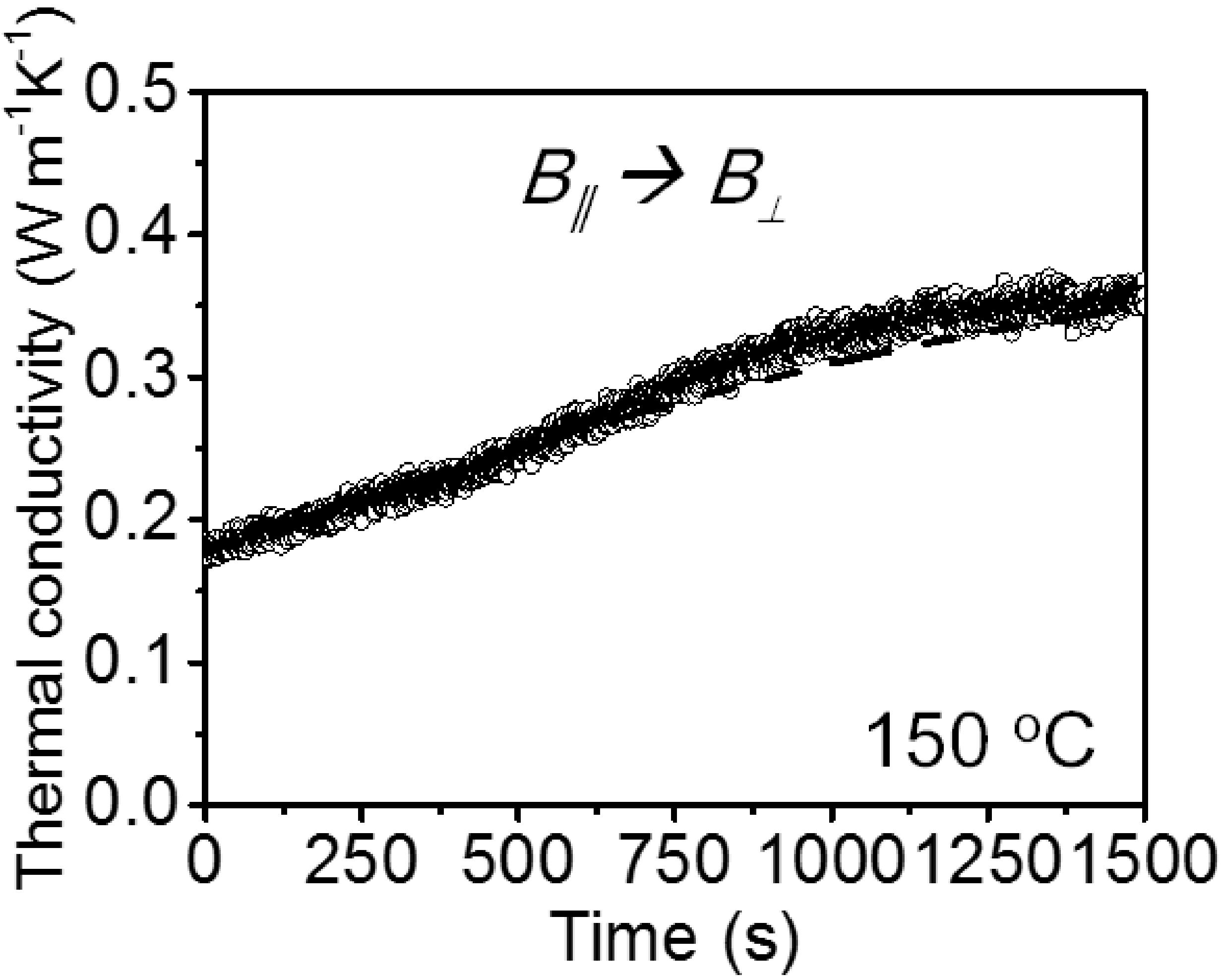
High thermal conductivity state is lost at high temperature; large hysteresis on cooling



Shin *et al.*, Macro Letters (2016)

Liquid crystal networks as thermally functional soft matter

- Reorientation of molecular order at T>Tg is relatively slow.



Conclusions

- Elastic constants, i.e., sound velocities and the minimum thermal conductivity model, can account for much of the variation in the thermal conductivity of amorphous polymers.
  - High thermal conductivity, 0.67 W m^{-1} K^{-1}, poly(vinylphosphonic acid calcium salt)
  - Low thermal conductivity, 0.06 W m^{-1} K^{-1} , in fullerene derivatives
  - Other cage structures do not produce such dramatically low thermal conductivities.
- Demonstrated that liquid crystals will be a rich subject for studies of “thermally functionally soft materials”. Search underway for higher contrast and faster response.